Modelling of scattering signal for direct PARAFAC decompositions of excitation-emission matrices

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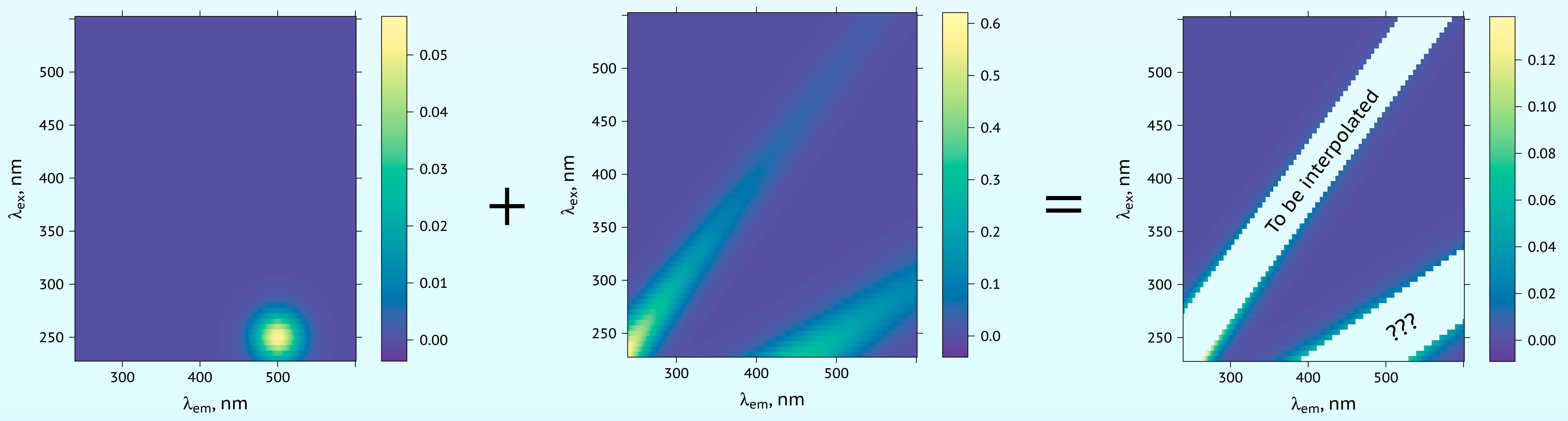
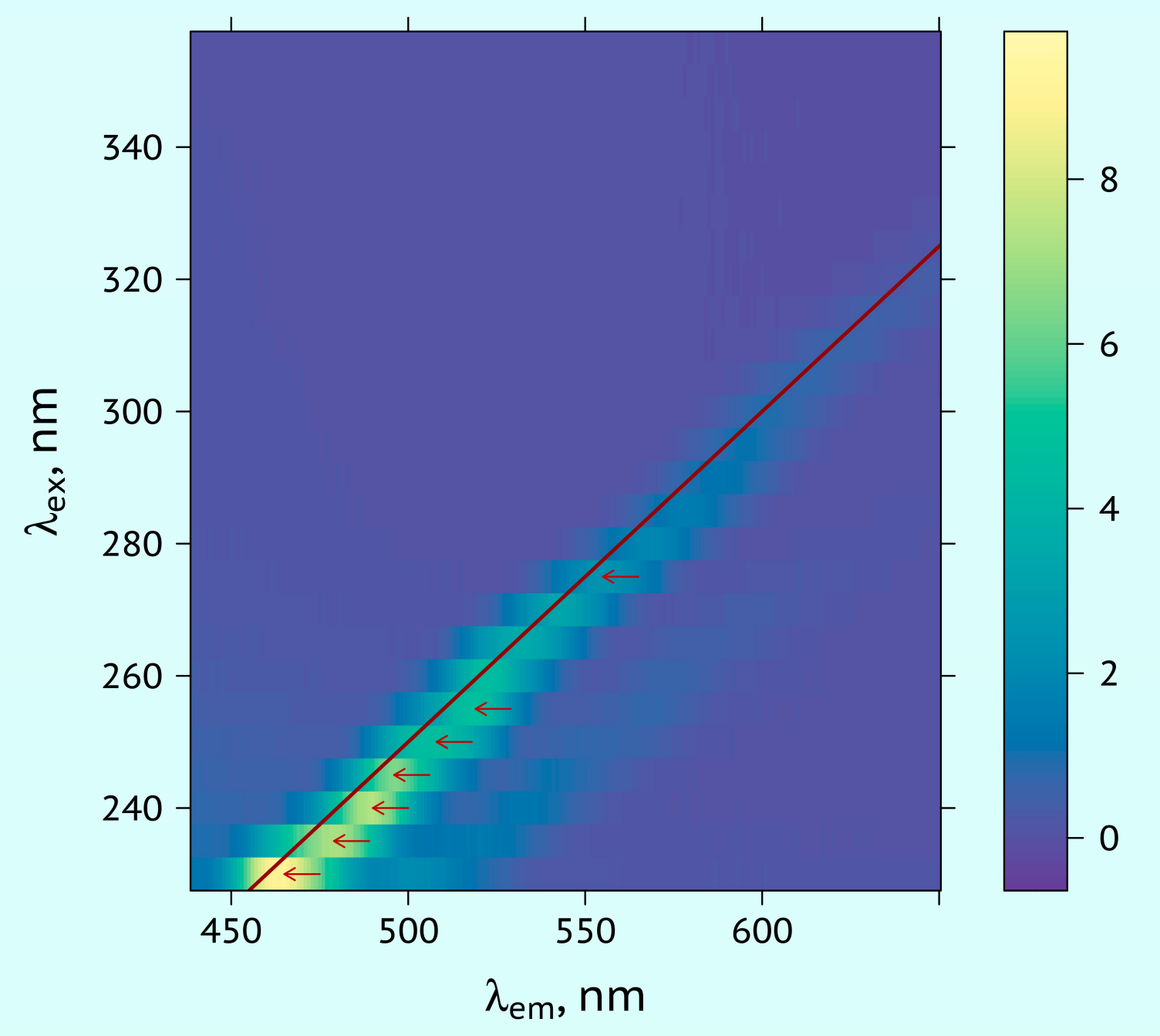
Motivation



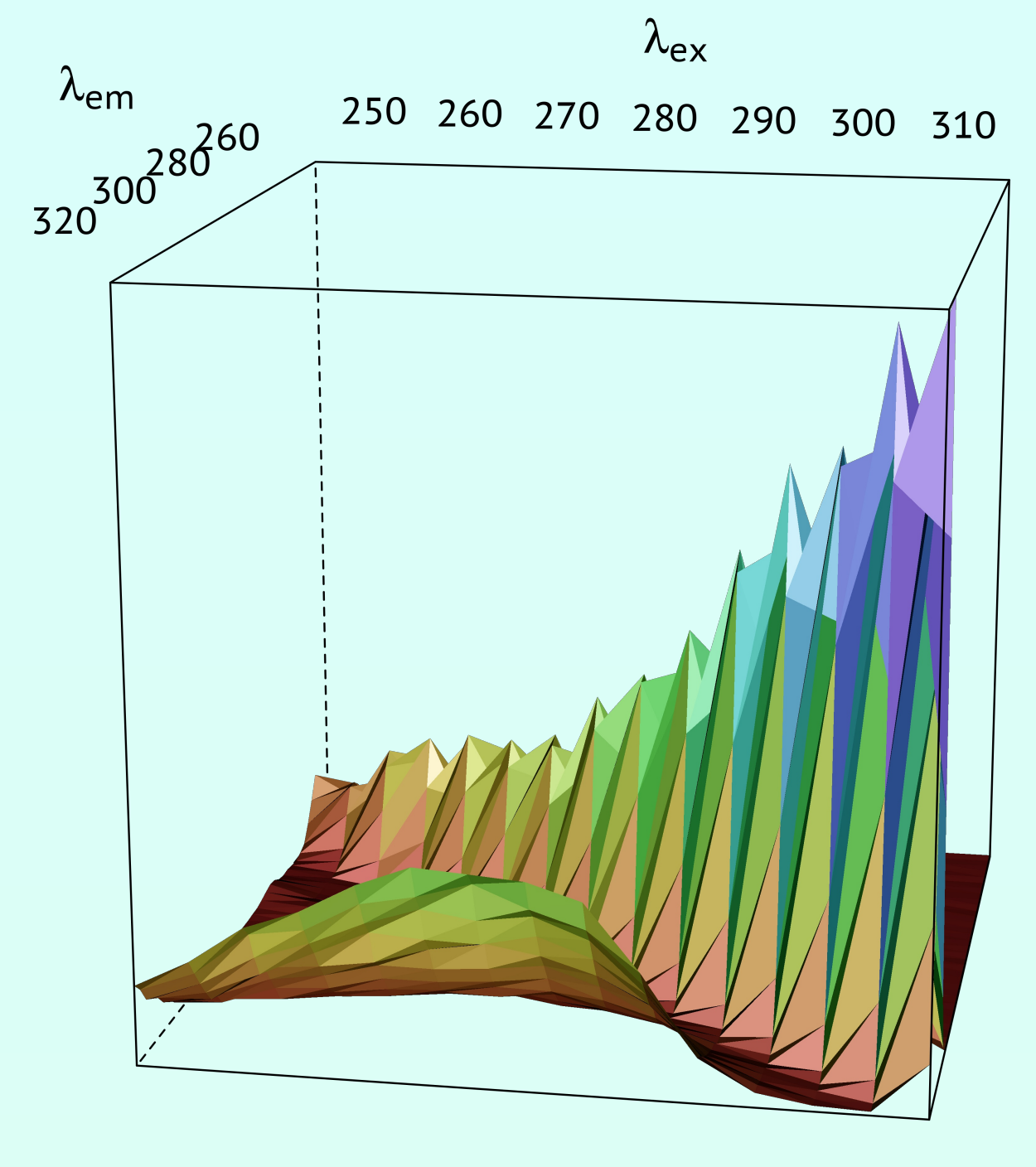
- PARAFAC is widely used in fluorescence spectroscopy
- Scattering signal doesn't adhere to PARAFAC assumptions
- Interpolation [1] of scattering areas is lossy
- Could scattering be modelled together with fluorescence?

What scattering may be

$$I(\lambda_{\mathrm{em}}, \lambda_{\mathrm{ex}}) = \underbrace{P(\lambda_{\mathrm{em}} - \lambda_{\mathrm{center}}, w)}_{\text{peak function}} \times \underbrace{\lambda_{\mathrm{ex}}^{-4}}_{\text{physics}} \times \mathrm{const}\ ?$$

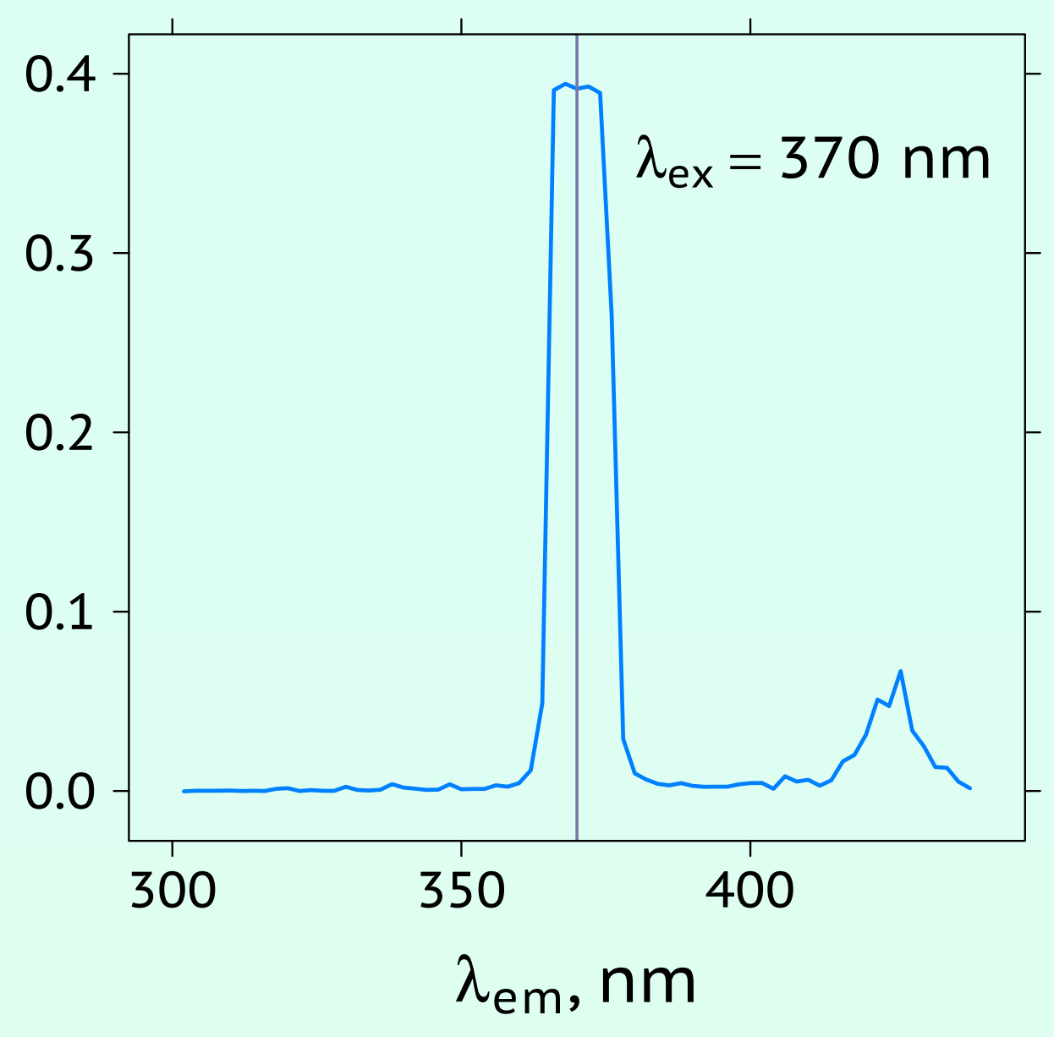


- Not a smooth line: wavelengths slightly miscalibrated
- Doesn't matter for fluorescence



[2], http://models.life.ku.dk/dorrit

- Not λ^{-4}: not calibrated for spectral sensitivity
- Unknown function of λ_{ex}



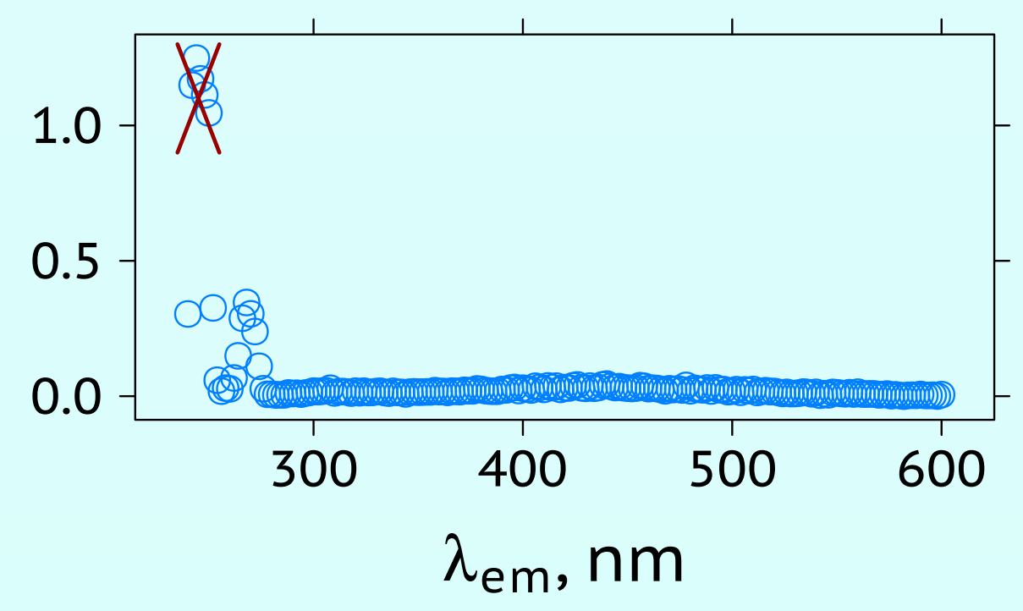
[1], Dogger bank dataset

- Not a Gauss/Lorentz/Voigt peak shape at all
- Scattering easily overflows detectors

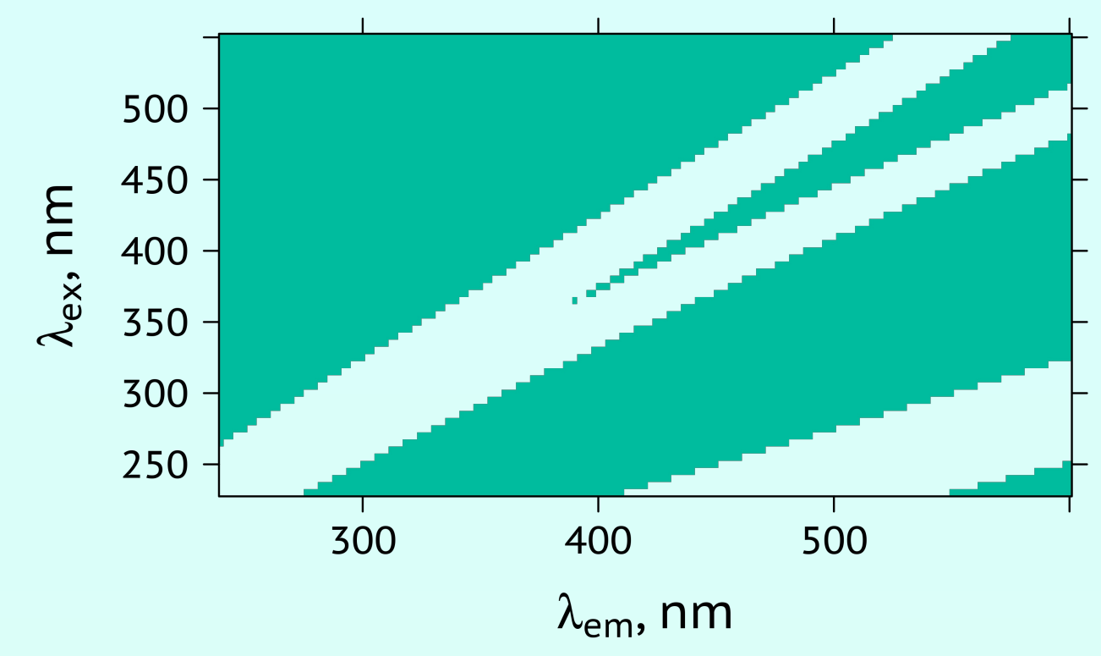
How to model scattering?

$$X_i(\lambda_j^{\mathrm{em}}, \lambda_k^{\mathrm{ex}}) = \underbrace{\sum_r A_{i,r} B_{j,r} C_{k,r}}_{\text{fluorescence, PARAFAC}} + \underbrace{\sum_r D_{i,r} S_{j,k,r}}_{\text{scatter, MCR}}$$

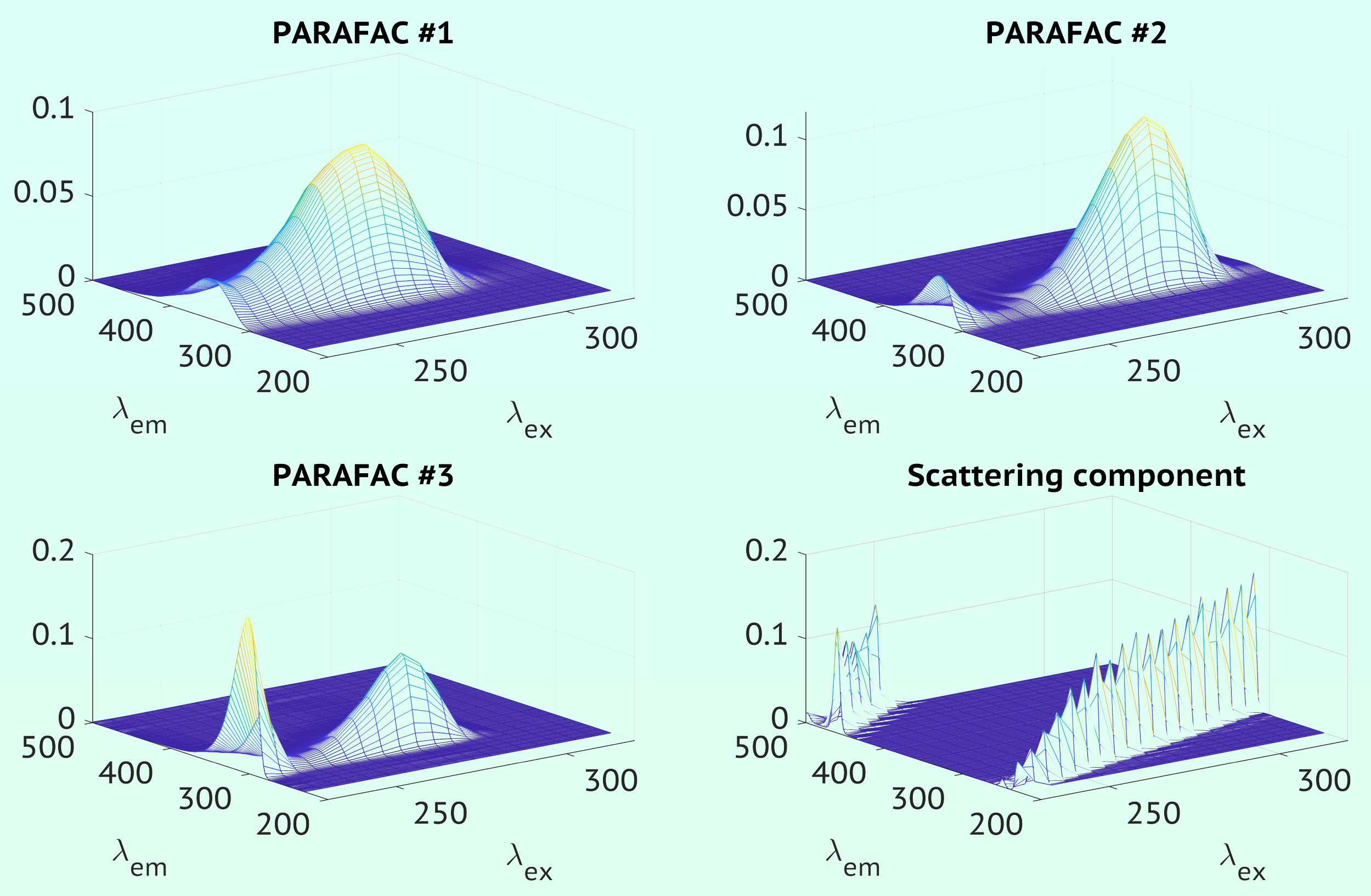
- Set overflowed values to missing



- Fit initial PARAFAC with scattering removed or interpolated
- Fix the MCR loadings to zeros outside scattering region



- Fit MCR and PARAFAC on each other's residuals, like [3]
- 1-3 MCR components needed, use MILES if needed



http://models.life.ku.dk/fluorescence

References

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[3] Tauler R.; Marqués I.; Casassas E.; Multivariate curve resolution applied to three-way trilinear data: Study of a spectrofluorimetric acid–base titration of salicylic acid at three excitation wavelengths, Journal of Chemometrics, 1998, 12, 55–75.

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